



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/SE97/00962 <b>(22) International Filing Date:</b> 3 June 1997 (03.06.97) <b>(30) Priority Data:</b> 9602817-0 19 July 1996 (19.07.96) SE <b>(71) Applicant:</b> SANDVIK AB (publ) [SE/SE]; S-811 81 Sandviken (SE). <b>(72) Inventors:</b> ROLANDER, Ulf; Tranebergs Strand 31, S-161 32 Bromma (SE). JOHANSSON, Hans; Körsbärsvägen 9:1305, S-114 23 Stockholm (SE). <b>(74) Agents:</b> ÖSTLUND, Alf et al.; Sandvik AB, Patent Dept., S-811 81 Sandviken (SE).		<b>(81) Designated States:</b> IL, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR OBTAINING A HIGH SURFACE FINISH ON TITANIUM BASED COATINGS  <b>(57) Abstract</b>  The present invention relates to a method for polishing coated cutting tools and wear parts, where at least the outer layer of the coating consists of TiN, TiC or Ti(C,N), to a high surface finish. An electrolytic method is used with an electrolyte consisting of perchloric (HClO <sub>4</sub> ) or sulphuric (H <sub>2</sub> SO <sub>4</sub> ) acid, 2-50 vol %, in methanol or other organic liquid. The method is easier to control than conventional mechanical methods and renders a high surface finish over the whole coated part.		

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Method for obtaining a high surface finish on  
titanium based coatings

The present invention relates to a method for polishing thin TiC, Ti(C,N) or TiN coatings, applied on e.g. cutting tools, to an extremely high surface finish using the electropolishing technique.

Thin wear resistant coatings, consisting of one or more layers of TiC, TiN, Ti(C,N) and/or Al<sub>2</sub>O<sub>3</sub>, are commonly applied on cutting tools and wear parts in order to increase their abrasive and chemical wear resistance. These coatings typically have a total thickness of 1-20  $\mu$ m and are applied using chemical vapour deposition (CVD), physical vapour deposition (PVD) and/or related techniques. The surface roughness of the coating after deposition depends on the roughness of the surface to be coated, on the total coating thickness and on the type of coating applied. In general, the surface of the coating will have at least the same roughness as the initial surface, the roughness will increase with coating thickness and a coating containing a layer of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> will be rougher than one containing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or Ti-comprising layers only.

One particularly interesting family of coatings is illustrated in Figs. 1a-b. Excluding some very thin bonding layers, the coating consists of an inner layer of Ti(C,N), x, deposited onto a cemented carbide cutting tool insert, an intermediate layer consisting of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, y, and a top layer of TiN, z. As deposited, this coating has unacceptable surface roughness, originating mainly from the rough  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> layer. This leads both to inferior performance and to a brownish rather unattractive colour of the insert. A smooth top layer of TiN generally has a shiny golden colour which is sought for cosmetic reasons. Today these problems are avoided

either by using thermodynamically less stable  $\kappa$ - $\text{Al}_2\text{O}_3$  instead of  $\alpha$ - $\text{Al}_2\text{O}_3$ , by mechanically polishing the  $\alpha$ - $\text{Al}_2\text{O}_3$  layer before depositing TiN or by mechanically polishing the TiN layer. The first method in many cases leads to inferior performance. The second method is an expensive two-step deposition process and the third method does not render the desired shiny golden colour.

Electrolytic smoothing or deburring is a commonly employed technique, especially for metallic materials. Two well-known processes are called electrochemical deburring and electropolishing. US 4,405,422 discloses methods for electrolytic deburring of copper or copper alloys and 4,411,751 of steel or aluminium alloys. In Swedish patent applications 9404326-2 and 9602278-5 methods for edge rounding of cutting tool inserts by electropolishing in an electrolyte containing perchloric ( $\text{HClO}_4$ ) or sulphuric ( $\text{H}_2\text{SO}_4$ ) acid in methanol are presented. Common for all these methods is that they are designed to produce smooth edges essentially without depth effect, each on a specific class of materials, and that they are applied prior to any coating process. Thus, any roughness originating from the coating itself is not eliminated.

It is an object of the present invention to provide a method for directly polishing the coating of cutting tool inserts, as well as drills, endmills and wear parts where at least the outermost layer of the coating consists of TiC, TiN or Ti(C,N). The method can be more carefully controlled than mechanical polishing and renders a high surface finish over the whole insert. In particular, a TiN coating applied onto a rough  $\text{Al}_2\text{O}_3$  layer may be polished to essentially eliminate the surface roughness and produce a shiny golden colour over the whole polished part.

It has surprisingly been found that by using methods similar to those disclosed in SE 9404326-2 and 9602278-5 but applying them after, instead of prior to, the coating process an extremely smooth surface with excellent cosmetic properties, which can not be made by mechanical methods, is obtained. Furthermore, since it is the coating and not the underlying material that is polished, the method is no longer limited to parts of cemented carbide and cermet alloys, but can also be applied to coated parts of e.g. high speed steel or ceramics.

Fig. 1 shows in cross section the nose (a) and clearance face (b) of a CVD coated cemented carbide cutting tool insert prior to treatment.

x - inner layer of  $\text{Ti(C,N)}$

y - intermediate layer consisting of  $\alpha\text{-Al}_2\text{O}_3$  and

z - top layer of  $\text{TiN}$ .

Fig. 2 shows in cross section the nose (a) and clearance face (b) of a CVD coated cemented carbide cutting tool insert treated for 15 seconds according to the invention.

Fig. 3 shows in cross section the nose (a) and clearance face (b) of a CVD coated cemented carbide cutting tool insert treated for 60 seconds according to the invention.

Fig. 4 shows in cross section the nose (a) and clearance face (b) of a CVD coated cemented carbide cutting tool insert treated for 120 seconds according to the invention.

According to the present invention the coated parts, having a single or multiple layer coating with  $\text{TiN}$ ,  $\text{TiC}$  or  $\text{Ti(C,N)}$  as outermost layer, are thoroughly cleaned e.g. by ultrasonic cleaning in methanol so that dust, loose particles, grease stains etc. that may affect the polishing result are removed from the surfaces. The parts are then submerged in the electrolytic bath and a

voltage is applied between the parts (anode) and a cathode. Strong agitation is carried out in order to obtain stable conditions with electrolyte flowing along all sides of the parts. The cathode should be made of an acid resistant material, e.g. platinum or acid resistant stainless steel.

The electrolyte shall contain 2-50 vol%, preferably 20-30 vol% perchloric ( $\text{HClO}_4$ ) or sulphuric ( $\text{H}_2\text{SO}_4$ ) acid, or a mixture thereof, in methanol. Methanol may be partly or fully substituted by more viscous fluids, e.g. butanol, glycerol or ethyleneglycol-monobutylether, in order to decrease the polishing speed or as a means for obtaining more stable conditions. The temperature of the electrolyte may be varied between room temperature and -60 °C, mainly in order to change the viscosity of the electrolyte.

The voltage shall be lower than 50 V but higher than 3 V, preferably 10-30 V. Generally a DC-voltage is used. But it is also possible to use pulsed or AC-voltage. The proper choice of voltage depends on the design of the equipment used, the degree of agitation obtained and the choice of electrolyte and temperature. The choice of electrolyte, temperature, applied voltage and polishing time should be adapted to the coating material and thickness, initial surface roughness and desired final thickness to obtain the best result. It is within the purview of the skilled artisan to determine these conditions.

Immediately afterwards the polished parts are rinsed, e.g. in methanol, in order to avoid corrosion caused by the electrolyte. With a correct choice of the different parameters described above a thin, highly viscous layer is formed at the interface between coating and electrolyte. Since the voltage drop occurs mainly across this layer the polishing speed will depend

strongly on its thickness. Therefore, on a rough surface, protruding parts will be polished faster than grooves, leading to a continuously decreasing surface roughness. On the other hand, if the choice of parameters is too far from the optimum, the viscous layer will never be formed or will be unstable, leading to oxidation or even pitting of the surface.

The method is suitable for mass production since large surface areas can be polished simultaneously with high polishing speed and extremely high accuracy and reproducibility.

#### Example

Cemented carbide inserts with a multiple layer coating as shown in Fig. 1 were electropolished for 15, 60 and 120 seconds, respectively, using an electrolyte consisting of 22 vol% sulphuric acid in methanol, cooled to -50 °C, and a DC-voltage of 20 volts. A 30 cm<sup>2</sup> platinum sheet was used as cathode and the electrolyte was stirred strongly using a magnetic mixer. As seen in Fig. 2, already after 15 seconds a substantial improvement of the surface roughness is obtained, especially over the nose. After 60 seconds, Fig. 3, the smoothness has been improved further at the clearance face. After 120 seconds, Fig. 4, protruding parts of the Al<sub>2</sub>O<sub>3</sub> layer have reached the surface of the TiN layer. An extremely smooth surface has been obtained over the whole insert, with TiN neatly filling out the grooves of the underlying Al<sub>2</sub>O<sub>3</sub> layer. Most of the TiN has been removed and it does no longer form a continuous layer. In this particular case, the process is actually self controlled. As the protruding parts of the electrically insulating Al<sub>2</sub>O<sub>3</sub> reaches the surface, the electrical contact to the islands of TiN in the grooves is cut off and the polishing stops. A similar effect is obtained when polishing a

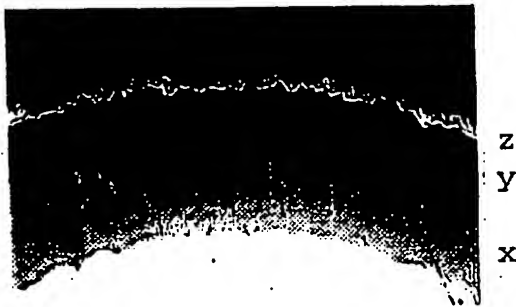
Ti-comprising coating on an electrically insulating ceramic part. However, the method works equally well on coated parts where all layers in the coating as well as the part itself is electrically conducting, though careful control of the polishing time may be more important in such a case.

Claim

1. Method for polishing coatings on cutting tools and wear parts, where the outer layer of the coating consists of TiC, TiN or Ti(C,N), to a high surface finish characterised in the following steps
- 5 providing an electrolyte of 2-50 vol% perchloric (HClO<sub>4</sub>) or sulphuric (H<sub>2</sub>SO<sub>4</sub>) acid, or a mixture thereof, in methanol or other organic liquid carrier
- submerging said coated parts into the electrolyte
- 10 providing an electrode of an acid resistant material, e.g. platinum or acid resistant stainless steel within the electrolyte and
- applying an electrical potential between the coated part (anode) and the electrode (cathode) for a period of
- 15 time sufficient to polish the outer layer.

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1a



1b



2a



2b



3a



3b



4a



4b

Fig. 1 - 4

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 97/00962

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C25F 3/16, C25F 3/22

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C25F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, JAPIO

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Dialog Informations Services, File 351, DERWENT WPI, Dialog accession no. 008678502, WPI accession no. 91-182522/25, (FURUKAWA ELECTRIC CO), "Electrolytic polishing of nickel-titanium alloy - using bath contg. trihydric alcohol, perchloric acid and monohydric alcohol", & JP,A,3111600, 910513, 9125 (Basic) --	1
X,P	US 5591320 A (ULF ROLANDER), 7 January 1997 (07.01.97), column 3, line 45 - column 4, line 52 --	1
A	WO 9113191 A1 (GORDON, ROY, G.), 5 Sept 1991 (05.09.91), page 5, line 13 - page 6, line 7, figure 2, claims 5,7 --	1

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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A	<p>Dialog Information Services, File 351,  World Patent Index 81-96, Dialog accession  no. 010641197, WPI accession no. 96-138150/199614,  CHEBOKSARY KHIPROM PRDN ASSOC: "Titanium nitride  film removal from surface of stainless steel  articles - comprises treatment in potassium hydrate  prior to treating the article in hot soln. of a  mineral acid";  &amp; RU,C1,2039851, 19950720, 920817, 199614 B</p> <p style="text-align: center;">--</p>	1
A	<p>Patent Abstracts of Japan, Vol 13, No 156, C-585,  abstract of JP,A,63-313000 (SEIKO INSTR &amp;  ELECTRONICS LTD), 21 December 1988 (21.12.88)</p> <p style="text-align: center;">--  -----</p>	1

INTERNATIONAL SEARCH REPORT  
Information on patent family members

01/09/97

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PC 97/00962

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US 5591320 A	07/01/97	EP 0777766 A IL 116352 D SE 9404326 A WO 9618759 A	11/06/97 00/00/00 13/06/96 20/06/96
WO 9113191 A1	05/09/91	CA 2075943 A DE 69127073 D EP 0516757 A,B FI 96874 B,C US 5202003 A US 5227036 A	24/08/91 00/00/00 09/12/92 31/05/96 13/04/93 13/07/93